POLYNUCLEAR COMPOUNDS FROM ACETYLENIC GLYCOLS

BY

DONALD EMANUAL PEARSON

B. S., University of Wisconsin, 1936

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY
OF ILLINOIS, 1940

URBANA, ILLINOIS

1940

POLYNUCLEAR COMPOUNDS FROM ACETYLENIC GLYCOLS

BY

DONALD EMANUAL PEARSON

B. S., University of Wisconsin, 1936

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE UNIVERSITY
OF ILLINOIS, 1940

URBANA, ILLINOIS

1940

ACKNOWLEDGMENT

The writer is greatly indebted to Dr. C. S. Marvel for his counsel and encouragement at every stage of this thesis.

Introduction

The acid hydration of substituted dienynes has been found to form unsaturated, cyclic ketones. Since the intermediate acetylenic alcohols and acetylenic glycols are synthesized in excellent yields, the above reaction seemed to offer a good method of obtaining hydroaromatic compounds of possible physiological interest or compounds which could be hydrogenated to carcinogenic hydrocarbons.

As the structures of the unsaturated ketones have recently been the subject of controversy, the question of the position of the double bond in relation to the ketone group, that is, conjugated or unconjugated, has been studied.[1] Still more recently, it has been suggested that the structures of these ketones are in reality of a cyclopentenone-spirane type rather than a cyclohexenone type.[2] This question has been investigated.

Discussion

The synthesis of cyclic ketones from the acid hydration of dienynes has been further extended.[3] From the hydration of the dienyne of 1-decalolcyclohexanolacetylene a crystalline ketone, $\Delta^{17,18}$-hexadecahydrochrysenone-6, was isolated and identified. A totally different compound, which was assigned a vinyl furan structure from its reactions, was formed along with the crystalline ketone. From the hydration of the dienyne of 2-decalolcyclohexanolacetylene another crystalline keone, $\Delta^{1,2}$-hexadecahydro-1,2-benzanthrone-3 was isolated and identified. Again, a by-product of the furan structure was obtained. From the hydration of the dienyne of 1,1′-didecalolacetylene, no ketone was obtained, but, rather, the vinyl furan product made up the entire yield.

The bromination and consequent dehydrobromation of 9-tetradecahydrophenanthrone yielded $\Delta^{13,14}$-dodecahydrophen-

anthrone-9, an unsaturated ketone *identical* with the ketone obtained by the hydration of $\Delta^{1,1}$-dicyclohexenylacetylene. If the fact is accepted that dehydrobromination of an *alpha* bromoketone yields an *alpha-beta* unsaturated ketone, it is established that the cyclic ketones from the hydration of the dienynes have conjugated carbon-carbon double bonds.

It was also shown that iodine monochloride absorption and reduction by zinc and acetic acid or reduction by the Clemmenson method varied with typical conjugated ketones and, consequently, could not be relied upon in deciding the question of conjugation or unconjugation.

A striking indication that the spirane structure may be the correct one was obtained by the study of the dibromides of 1-decalone and of the supposed 9-tetradecahydrophenanthrone from the hydration and consequent hydrogenation of $\Delta^{1,1'}$-dicyclohexenylacetylene. It would be expected that, since the dibromide of 1-decalone dehydrobrominated to 5,6,7,8-tetrahydro-1-naphthol, the dibromide of 9-tetradecahydrophenanthrone would behave similarly. On the contrary, the latter dibromide dehydrobrominated to a crystalline unsaturated bromoketone and yielded no trace of a phenolic product.

Summary

1. The study of polynuclear compounds from acetylenic glycols has been extended to compounds with chrysene, 1,2-benzanthracene, and picene ring structures.

2. It has been proved that the unsaturated ketones obtained from the acid hydration of dienynes have conjugated systems.

3. Evidence has been advanced to make the possibility of the formation of spirane compounds rather than cyclohexenone compounds from the hydration of dienynes a likely one.

Bibliography

[1] Linstead and Walpole, J. Chem. Soc., **1939**, 842.

[2] Bogert, 99th Meeting, Amer. Chem. Soc., Cincinnati, Ohio, 1940.

[3] Marvel, Mozingo and Kirkpatrick, J. Am. Chem. Soc., **61**, 2003 (1939).

Vita

The writer was born in Madison, Wisconsin, on June 21, 1914. He attended a grammar school of Madison, Wis., and graduated from Madison Central High School in 1932. He received the Bachelor of Science degree from the University of Wisconsin in 1936. From 1936 to the present date he has been an assistant in organic chemistry at the University of Illinois while studying for the degree of Doctor of Philosophy.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549820_0130